The effect of chloride ions on the optical properties of TeO_2-CuO-$CuCl_2$ glasses

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The glasses with composition $65TeO_2$-$(35 - x)$CuO-xCuCl_2 (x = 0, 1, 2, 3, 4, 5 mol%) were prepared by a melt quenching technique and thin films of different thicknesses were made by blowing. The optical energy gap was studied and its variation with composition is discussed in terms of the effective role played by chloride ions which reduce the non-bridging oxygen ions and modify the structure of the network. The infrared spectra of all these glass samples at room temperature, recorded between 200 and 2400 cm^{-1}, are discussed in terms of anti-symmetric vibrations of the heteronuclear atoms.

1. Introduction

For many years there has been considerable doubt about the existence of TeO_2 in a truly glassy state and indeed many workers claimed that such a material could not exist. Glasses having TeO_2 as a main component have been produced over a long period [1] and found to have a low transition temperature. TeO_2 is frequently included in optical glasses with high refractive index and the known chemical stability makes them useful as optical components.

The optical absorption in solids takes place in a number of ways, all of which involve the coupling of the electric vector of the incident radiation to dipole moments in the material and the consequent transfer of energy, for example, by ligand fields in which the absorption takes place by internal transitions between d-shell electrons. The broad, flattened maxima in the absorption spectra arise in glasses as a result of structural disorder which develops in melts on account of thermal vibrations and the freezing in of various vibrational states. It can also be argued that the disturbance of the symmetry of the ligand field results in a disordering of the energy levels of the d-electrons. Thus the absorption band grows wider and sometimes it develops a fine structure. The absorption can also arise by the transfer of electrons from neighbouring atoms to the transition metal (TM) ions and vice versa in what is called the charge transfer band.

The first row of transition metals owe their optical properties to excitation of the 3d electrons. The absorption bands are extremely broad and sensitive to changes in co-ordination and symmetry. Kozhurkharov et al. [2, 3] have discussed binary and ternary tellurite glass systems containing TM oxides. They have suggested that the melting condition of tellurite glasses having TM ions (volatility and low viscosity) and the variation in the glass formation region depends on the nature of the modifier and the type of phase diagram. Binary [4] and ternary [5–8] tellurite systems with heavy metal oxides and transition element halides [3] have also been successfully studied. The optical absorption in WO_3-CaO-TeO_2 glasses as well as in pure TeO_2 and TeO_2-WO_3 glasses has already been reported [9].

The aim of the present work is to study the optical absorption in $65TeO_2$-$(35 - x)$CuO-xCuCl_2, a glass system with x = 0, 1, 2, 3, 4, 5 mol% and whose properties have not previously been reported in the literature.

For many amorphous materials, Urbach [10] assumed that the absorption coefficient $\alpha(\omega)$ was an exponential function of photon energy $\hbar\omega$ and takes the form

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e) \qquad (1)$$

where α_0 is constant, $\hbar$ is the reduced Planck constant and E_e is an energy which is sometimes interpreted as the width of the tails of localized states in the band gap which are associated with the amorphous nature of the material, and ω is the angular frequency of incident radiation. This relation is also found to be applicable for many glassy or amorphous semiconductors over a wide range of absorption edges while for high values of absorption coefficient $\alpha \gg 10^4 cm^{-1}$, a relation proposed by Tauc et al. [11] and more generally deduced by Davis and Mott [12] is found to hold

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n/\hbar\omega \qquad (2)$$

B is constant, n is an index which can assume values of 2, 3, 1/2, 3/2 depending upon the nature of the transition responsible for absorption, ω is the radial frequency and E_{opt} is defined as the optical band gap. For many glasses [13,14], in Equation 2, the value of n = 2 is found to give good results and in this case corresponds to indirect transitions in such materials when the electron wave vector k can no longer be well-defined.

2. Experimental work
2.1. Glass preparation
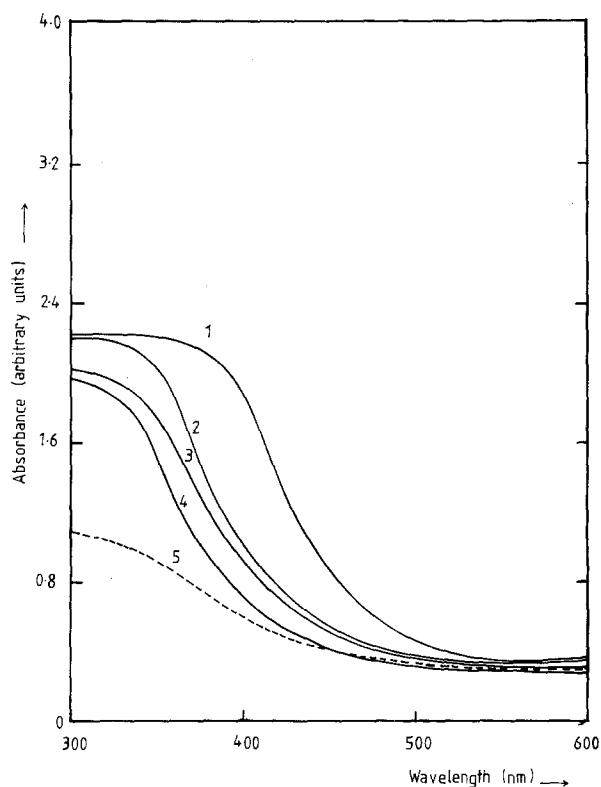Glasses of the TeO_2-CuO-$CuCl_2$ system were prepared from chemically pure grades of materials in

Figure 1 Variation of optical absorbance with wavelength for five glass samples.

Figure 2 Variation of optical absorbance with wavelength for a binary (TeO_2–CuO) glass film.

alumina crucibles. A typical melt used some 30 g of material. In order to reduce a tendency to volatilization, the mixture was initially heated for 1 h in a furnace maintained at 300° C. The crucible was then transferred to an electric furnace preheated to a temperature of 950 to 970° C and held at this temperature for 2 h. The melt was stirred from time to time using an alumina rod to improve homogeneity. Thin glass films which were necessary for optical measurements were prepared by dipping an alumina tube into a molten glass and gathering a small amount of semi-molten glass on the end of the tube and blowing it into air. The remaining melt was finally poured on to a clean steel plate and cast into disc-shaped samples of 1.5 to 2 cm diameter and about 2 to 3 mm thick. The unannealed glass samples were ground into fine powder which was used in the infrared measurements.

2.2. Optical absorption measurements

The thicknesses of the thin blown films for various glass compositions lying in the range 1.66×10^{-4} to 2.28×10^{-4} cm were measured using a Sigma Comparator. All the thin films were unannealed for optical measurements which were carried out on these films at room temperature, in the wavelength range 300 to 600 nm, using a Perkin-Elmer Spectrophotometer Model 402. The values of absorbance A in arbitrary units for each glass composition were determined from Fig. 1 for the ternary glass TeO_2–CuO–$CuCl_2$ and from Fig. 2 for the binary glass TeO_2–CuO. The optical absorption coefficient $\alpha(\omega)$ which is a function of wavelength can be calculated from the optical absorption spectra by using relation
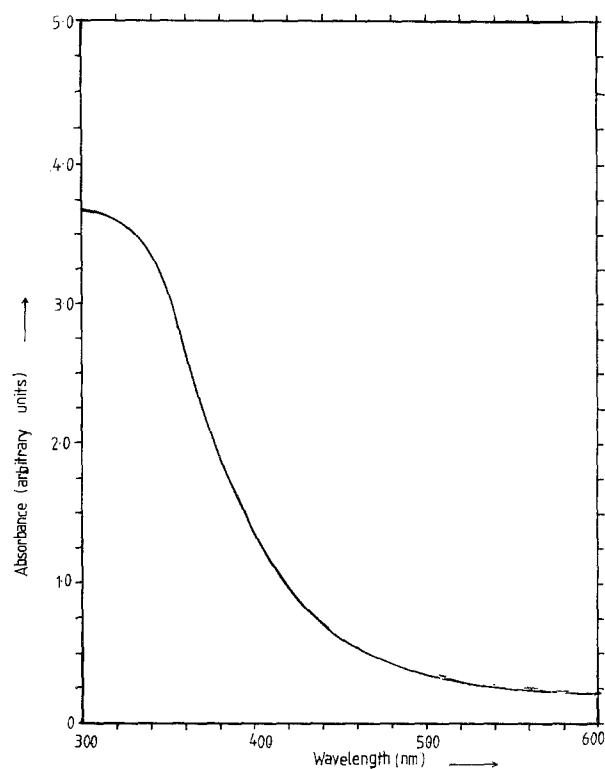
$$\alpha(\omega) = 2.303 A/d \qquad (3)$$

where d is the thickness of the sample and A is the absorbance in arbitrary units mentioned above which is defined as

$$A = \ln (I_0/I_t) \qquad (4)$$

where I_0, I_t are the intensities of the incident and transmitted beams. Table I shows the compositions of all glasses reported in this paper. X-ray diffraction measurements were made using a Debye–Scherrer powder camera. Only diffuse diffraction rings were seen, showing the glassy nature and giving no evidence of crystallinity.

3. Discussion of results

The compositions of the glass samples and some of their characteristic parameters are listed in Table I. Figures 1 and 2 show the optical absorption spectra for ternary and binary glasses, respectively, at room temperature (300 K) for samples having different thicknesses. It is observed that the optical absorption edges shift to higher energies as the $CuCl_2$ content is increased. It is clear from Figs 1 and 2 that there are no sharp absorption edges and this is a characteristic of a highly disordered material. The absorption spectra in Fig. 1 show that the edge varies systematically as the percentage of $CuCl_2$ is increased.

TABLE I Some characteristic energy parameters of six copper tellurite glasses containing $CuCl_2$

No.	Sample	$CuCl_2$ content (mol %)	E_{opt} (eV)	E_e (eV)
1	T_0	0	2.01	0.48
2	T_1	1	2.08	0.57
3	T_2	2	2.15	0.51
4	T_3	3	2.23	0.53
5	T_4	4	2.35	0.58
6	T_5	5	2.43	0.66
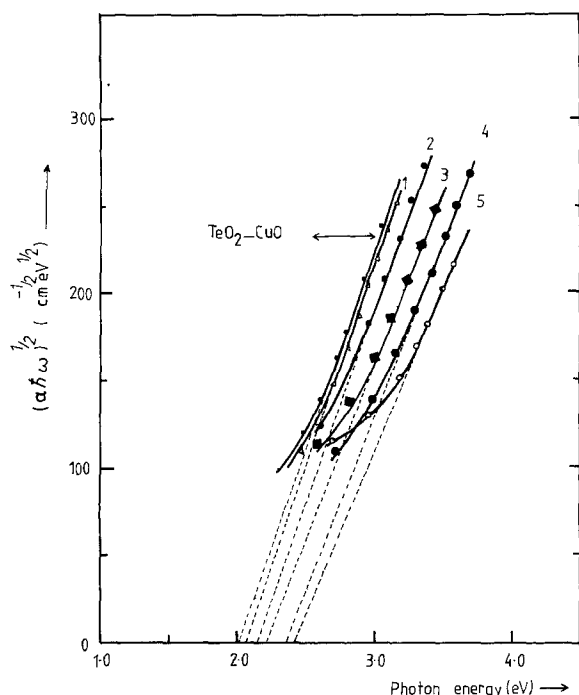
Figure 3 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for TeO$_2$-CuO-CuCl$_2$ glasses.

Figure 4 Optical energy gap E_{opt} as a function of CuCl$_2$ content.

The optical data obtained from Figs 1 and 2 are plotted in Fig. 3 as the quantity $(\alpha\hbar\omega)^{1/2}$ against the photon energy $\hbar\omega$ and the values of E_{opt} are determined by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$. The graphs show straight lines with some deviations at lower photon energies which according to Redfield and Afromowitz [15] were due to the imperfections in the materials. The general trend is not obeyed by glass 5 having the greatest content of CuCl$_2$. Figure 4 shows that the optical gap increases with the increase of CuCl$_2$ content. It has already been found that the incorporation of a strong oxidizing agent such as chlorine [16] and iodine [17] can substantially affect the reduced valency ratio and the electronic properties of transition metal phosphate glasses. Also the effect of chlorine on the optical absorption has been observed in the PrCl$_3$-GeO$_2$ glass system [18] where a sharp fundamental optical absorption edge and sharp absorption peaks were observed with increase of PrCl$_3$ content. It was observed in this system that the values of E_{opt} decrease with a small increase in the concentration of PrCl$_3$ but further increase again with the further addition of PrCl$_3$ and chlorine becomes less effective and acts as a dispersed oxidizing agent making Pr^{3+} ions more dominant and effective in increasing the optical gap. Hogarth and
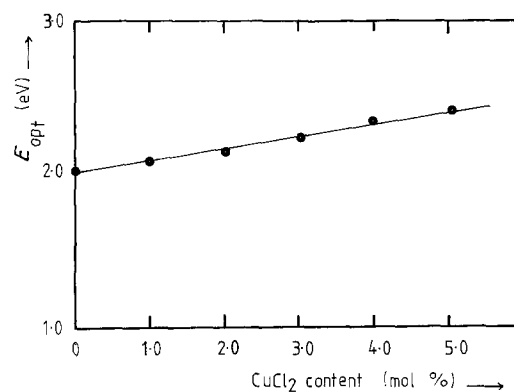
Popov [16] reported that all parameters measured related to Cu^{2+} concentrations decreased with a small increase in CuCl$_2$ to a range up to 4 mol % in copper phosphate glasses and increased again for further additions of CuCl$_2$. Mc Swain et al. [20] have reported that the change of oxygen bonding in the glassy network, for instance the formation of non-bridging oxygen, changes the absorption characteristics.

In the glass system under investigation, it is observed that the structure of the glassy network is also affected as the chloride ions replace the non-bridging oxygen ions. The values of E_{opt} increase continuously with the increase of CuCl$_2$ up to 5 mol % and show no such behaviour as predicted by previous workers [16, 17]. The increase in E_{opt} in this system can be explained by assuming that the addition of chlorine modifies the band characteristics in a systematic manner by reducing the concentrations of Cu^{2+} ions and with more than 3 mol % CuCl$_2$, the role of the chloride ions becomes more dominant causing a significant increase in E_{opt}. The values of E_{opt} in the present study lie in the range 2.08 to 2.43 eV for glasses with 1 to 5 mol % CuCl$_2$, respectively, and 2.01 eV for the binary glass [65TeO$_2$-35CuCO (mol %)] which is taken as the reference glass, and the results of other glasses are compared with it. This increase in E_{opt} is attributed to the decrease in the concentrations of non-bridging ions with the increase of CuCl$_2$ content. The curves giving the relation between ln α and $\hbar\omega$ are shown in Fig. 5. The widths of the band tails E_e of localized states in Equation 1 are calculated from the slopes of straight portions of the curves (Urbach plots) between the points (a) and (b) shown in Fig. 5 and their numerical values are recorded in Table II. Different views have been expressed about this exponential dependence but its exact origin is not

TABLE II Characteristic infrared absorption band positions for tellurite glasses

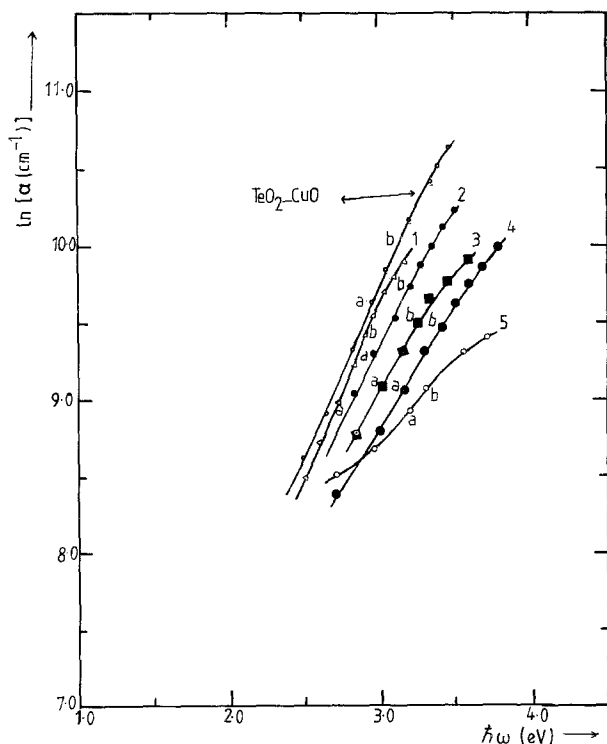| No.	Samples	CuCl$_2$ content (mol %)	Band positions (cm^{-1})			
–	TeO$_2$(crystal)	–	230	345	–	660–670, 775
–	CuCl$_2$(crystal)	–	230	275	–	–
1	T$_0$	0	230	310, 370	405, 455–475	675–695
2	T$_1$	1	230	–	450–500	650–700
3	T$_2$	2	230	–	450–500	650–700
4	T$_3$	3	230	–	350–359	662–700
5	T$_4$	4	230	259–310	–	635–695
6	T$_5$	5	230	259–310	570	645–700

Figure 5 Absorption coefficient as a function of photon energy for TeO_2–CuO–$CuCl_2$ glasses.

clearly known. Tauc and Zanini [11] believe that the densities of states in the band tails which control the electronic transitions between localized states are exponentially dependent on the photon energy. Dow and Redfield [20] suggested that the tailing may arise from the random fluctuations of the internal disorder in many amorphous solids.

Mott and Davis [14] reported that the slopes of the observed exponential edges obtained from Equation 1 are very much the same as in many semiconductors and the values of E_e for a range of amorphous semi-

conductors lie between 0.045 and 0.67 eV. The values of E_e in our present work also lie in the range 0.5 to 0.66 eV and are in very good agreement with the prediction of Mott and Davis [14], so it can be assumed that the added chloride ions are widely and thinly dispersed in copper tellurite glasses and do not form clusters in the system. From the above discussion, it can be said that the nature of bonding in copper tellurite glasses containing $CuCl_2$ is somewhat different from the other related systems of glasses reported earlier [16–18].

Some clues to the bonding in complex glass systems may be obtained by making infrared absorption measurements which are known to provide an important tool in studying the structure of gaseous molecules and organic substances. The applications of these infrared techniques to glassy materials is limited, mainly due to the complicated and random structure of the glassy state. The results on the infrared transmission of the glasses together with that of TeO_2 (crystalline) and $CuCl_2$ (crystalline) in the range 200 to $2400 \, cm^{-1}$ recorded at room temperature with a Unicam SP200 infrared spectrophotometer which was operated in the double beam mode, are shown in Fig. 6.

The unannealed glass samples were ground in a clean mortar into a fine powder and then a small amount of glass powder was weighed, mixed and ground with KBr in the ratio 1 : 20 to make samples suitable for the transmission of infrared radiation. The thin pellets were formed by pressing the mixture at 15 ton under vacuum for 3 to 5 min. The numerical values of the detectable absorption band maxima in the infrared spectra of these glasses are compiled in Table II. All glasses of our ternary system show great similarities in their general shape of absorption spectra.

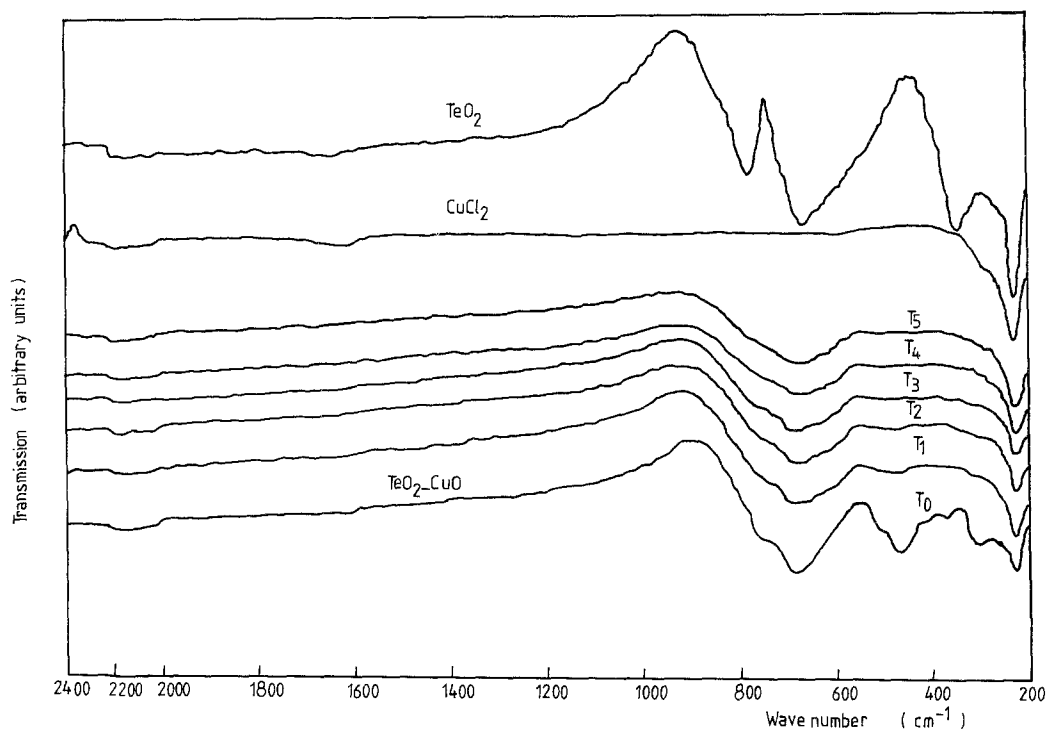It is observed that the positions of absorption bands

Figure 6 Infrared absorption spectra of TeO_2; $CuCl_2$ and TeO_2–CuO–$CuCl_2$ glasses.

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in the TeO_2 spectrum are in very close agreement with those reported by earlier workers [9, 21–23]. These values show the existence of TeO_2 in the glass under study. Al-Ani et al. [9] attributed the absorption to symmetrical vibrations in the O–Te–O bond while Sunandana [24] reports this to be antisymmetric in TeO_2–CuO–V_2O_5 glasses. In the present work, it is evident from the spectra of binary TeO_2–CuO glass that the transmission peaks which appeared in the TeO_2 spectra are lowered, the absorption bands are slightly broadened and shoulders at 400, 425, 484, 500 and 740 cm^{-1} appear due to deformation generated by the addition of CuO. The absorption band at 230 cm^{-1} which appears in all glasses and in both crystalline TeO_2 and $CuCl_2$ is known to be at the fundamental frequency. The band for CuO which should appear at 620 cm^{-1} as predicted by Hogarth and Moridi [25] is not detectable in the copper tellurite glassy network. It is probably buried in the broad transmission region at 600 to 650 cm^{-1}. A small amount of $CuCl_2$ (1 mol%) greatly affects the binary structure of TeO_2–CuO glass. Its presence increases the density of Cu^+ ions due to the infusion of chloride ions and so the bonds between Te–O–Cu which are minimally bent are considerably stretched, thereby creating maximum internal disorder which is characteristic of non-crystalline materials. The main frequencies in the range 635 to 775 cm^{-1} may be ascribed to the stretching of Te–O–Cu bonds. The absorption bands at 2000 to 2230 cm^{-1} which are observed in all these glass series are believed to be associated with an OH group due to a small amount of water trapped in the glasses. The bands at 1580, 1375 and 2330 cm^{-1} are more likely to be due to overtones. So because of deformation and internal disorder caused by bending and stretching of bonds, the present spectra can be generally attributed to anti-symmetric vibrations of heteronuclear atoms.

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